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Environmental Effects on Intermetallic Compounds: A Guide to the Literature

Saul Isserow

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Saul Isserow

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U.S. Army Research Laboratory
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13. ABSTRACT *(Maximum 200 words)*

This report is a guide to the literature on environmental effects on intermetallic compounds; primarily the aluminides of nickel, titanium, iron, and niobium. The guide relies heavily upon the proceedings of recent conferences. Brief technical discussions introduce the various topics and lead to specific sources of information. Various relevant review articles are also listed.

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Introduction

This report is a guide to the literature on environmental effects on intermetallic compounds. These compounds are being developed for high temperature applications to extend service temperatures beyond the range currently served by nickel-base superalloys for gas turbines (~ 1100°C). Increased material capabilities are required for programs directed at substantial advances in the state-of-the-art: Integrated High Performance Turbine Engine Technology (IHPTET), Joint Turbine Advanced Gas Generator (JTAGG), and the National Aerospace Plane (NASP). The emphasis is on aluminides of nickel, titanium, and, to a more limited extent, iron and niobium. Those interested in the intermetallics will be aided by the information assembled here in gaining familiarity with the subjects of interest.

This report makes no pretense of providing a comprehensive survey of the entire literature on the broad topic. The intent is to enable the reader/user to begin tracking all the previous work on a specific subject of interest. The publications cited here will indeed lead the reader to significant work on that subject. These citations serve as starting points.

Intermetallics have had surges of interest since World War II. Only in the last five or, at the most, ten years has environmental behavior received priority consideration for potential applications. In fact, it is now clear that the failure to recognize environmental embrittlement led to earlier dismissal of some intermetallics because of brittle behavior that was believed to be inherent for these compounds. The development of the intermetallics initially emphasized mechanical behavior such as strength and ductility. Substantial progress resulted from the recognition of the crucial role of grain boundaries; their weaknesses can be the cause of decohesion. Significant advancement in environmental durability is associated with the establishment of the impairment of grain boundary cohesion by contaminants such as oxygen or hydrogen picked up from the atmosphere.

This report relies heavily on the proceedings of various recent conferences sponsored by technical societies such as Materials Research Society (MRS), The Materials Society (TMS), and American Society for Metals (ASM). These proceedings have the obvious advantage of providing many valuable presentations in a single package including references to published (and, at the time, unpublished) research. In addition, many of the authors having been active in the field provide their assessments or distinctive points of view.

The initial section of this guide lists various review articles on the overall subject and on the subjects of alloy design, environmental behavior, and aerospace applications. Detailed attention is then given to the two categories of environmental behavior based on the temperature regimes: ambient temperature with emphasis on corrosion-related embrittlement and high temperature.

In each regime the aluminides are presented in the sequence iron, nickel, and titanium. For high temperature three paragraphs on niobium arbitrarily precede the others. References to other (nonaluminide) intermetallics are scattered in locations determined by the subject matter.

As an indicator of the level of interest in these compounds, it is worth noting that they were the subject of symposia last fall (1992) at the Materials Week and at the MRS meeting. When available, the respective proceedings will, of course, provide additional guidance for ongoing and projected research.

Citations of conference proceedings are concisely identified within the text through the conference site; the key to these references is the list following the text (see Symposium Proceedings). Other citations refer to the alphabetized list at the end (see References - Journals). It should be noted that the citations are not necessarily indicative of priority.

Introductory minitutorials are provided on various subjects to set the stage for the citations.

Broad Reviews

Reviews are available to provide background either on the overall subject of intermetallics or on specific technical subjects or groups of compounds. The field is very active; hence, any state-of-the-art review contains some information that is obsolete by the time it is presented or published. Such ongoing obsolescence need not be a drawback. Each review has merit for its presentation of historical development and the point of view and concerns of the author(s). An interesting point is the attention, or lack of it, to environmental behavior. A full treatment of intermetallics can be expected in two forthcoming books: one is edited by Sikka and Stoloff, and the other is edited by Westbrook and Fleischer.

An excellent starter is the review by Fleischer, Dimiduk, and Lipsitt (1989) including 210 references. One of the attractive features is the series of separate sections assessing "Well-Studied Materials." A more concise review is available by Taub and Fleischer (1989) with 45 references.

Alloy design considerations are covered by Takasugi (MRS IV, (12), 75 references, p. 403) with emphasis on intergranular fracture. Related considerations are applied even more specifically by Takeyama and Liu to elevated temperature environmental embrittlement with special reference to $L1_2$ structures of Ni_3Al and Ni_3Si (San Diego, CA, (10), p. 538). Alloy design presentations by Cottrell and Cahn at Euromat 91, held in Cambridge, UK in July 1991, are assumed to be of great relevance but copies have not yet been obtained.

Environmental behavior is reviewed in the following conference presentations:

- Meier: Cleveland, OH (1), 29 references, p. 1
- Liu and McKamey: Indianapolis, IN (3), 72 references, p. 113
- Meier: Les Embiez, France (5), 62 references, p. 1
- Takeyama and Liu: San Diego, CA (10), 35 references, p. 538
- Meier and Pettit: San Diego, CA (10), 38 references, p. 548

Liu's papers are on embrittlement; the three papers by Meier deal with oxide growth.

More concise, but very useful, treatments of hydrogen embrittlement (HE) and oxidation are included in the two reviews at the May 1992 Tri-Service Corrosion Conference (13) at Plymouth, MA given by Duquette and Stoloff and Meier and Pettit.

The following publications emphasize **aerospace applications** of the respective aluminides:

DIMIDUK and MIRACLE. *Directions in High Temperature Intermetallics Research*, MRS III (11), p. 349.

ANTON and SHAH. *High Temperature Ordered Compounds for Advanced Aero-Propulsion Applications*, MRS III (11), p. 361.

FROES. *Structural Intermetallics*, 1989, p. 6.

FLEISCHER and TAUB. *Selecting High Temperature Structural Intermetallic Compounds: The Materials Science Approach*, 1989, p. 8.

ANTON, SHAH, DUHL, and GIAMEI. *Selecting High Temperature Structural Intermetallic Compounds: The Engineering Approach*, 1989.

KIM. *Intermetallic Alloys Based on Gamma Titanium Aluminide*, 1989, p. 24.

KIM and FROES. *Physical Metallurgy of Titanium Aluminides*, Indianapolis, IN (3), 114 references, p. 465.

LARSEN et al. *Aluminides for Aerospace Applications*, Indianapolis, IN (3) 50 references, p. 521.

KIM and DIMIDUK. *Progress in the Understanding of Gamma Titanium Aluminides*, 1991, p. 40.

DAROLIA. *NiAl Alloys for High Temperature Structural Applications*. 1991, p. 44.

FROES et al. *Advanced Aerospace Metals Requirements and Characteristics - An Overview*, Paris, France (9), p. 1.

DUQUETTE and STOLOFF. *Aerospace Applications of Intermetallics*, Paris, France (9), p. 289.

KHAN et al. *Intermetallics for Structural Applications*. Liège, Belgium (6), p. 152.

LARSEN, WILLIAMS, BALSONE, and STUCKS. *Titanium Aluminides for Aerospace Applications*. Indianapolis, IN, (3) p. 521.

MacKAY, BRINDLEY, and FROES. *Continuous Fiber-Reinforced Titanium Aluminum Composites*, 1991.

ASHLEY. *Titanium Aluminides: Tough Materials for Tomorrow's Engines*, 1991.

DIMIDUK, MIRACLE, and WARD. *Development of Intermetallic Materials for Aerospace Systems*, London, England (7), p. 367.

BEDDOES, WALLACE, and DeMALHERBE. *The Technology of Titanium Aluminides for Aerospace Applications*, 1992.

NAKA, THOMAS, and KHAN. *Potential and Prospects of Some Intermetallic Compounds for Structural Applications*, London, England (7), p. 291.

YAMAGUCHI. *High Temperature Intermetallics with Particular Emphasis on TiAl*, London, England (7), p. 299.

Behavior At Ambient Temperature And Corrosion-Related Embrittlement

Materials can be impaired by exposure to media in which water is present as an oxidizing agent at ambient temperature, either as liquid or as a constituent of the atmosphere. A liquid environment introduces the possibilities of stress corrosion, pitting, and passivation. Oxidation of metal by water in any form entails a concurrent reduction generating elemental (zero valent) hydrogen in some form. This hydrogen is capable of embrittling the metal substrate. Such embrittlement poses a potentially serious limitation on the structural application of intermetallic compounds which, at best, seem to be always on the ragged edge of brittle behavior. As indicated above, the unrecognized HE phenomenon previously led to premature dismissal of intermetallics as inherently too brittle.

This phenomenon has been receiving considerable attention, especially, but not exclusively, in the titanium aluminides. This attention to the titanium compounds is related to (and abetted by) the thorough studies of the interaction of more conventional titanium alloys with hydrogen extending even to the deliberate addition and removal of hydrogen in some process sequences.

Overviews of HE in intermetallics are available in several publications. The tri-service review (13) by Duquette and Stoloff is a useful starter in organizing the affected intermetallics on the basis of crystal structure and presenting representative test data. A broader review, including 33 references, is presented by Stoloff (Jackson, (4), p. 483). Stoloff also published a shorter review with 20 references in the December 1988 Journal of Metals as part of a set of reviews on Environmental Effects on Advanced Materials. Another review by Stoloff, Shea, and Castagna assembles (for nickel, iron, and titanium aluminides) the data clarifying mechanisms and contributive factors with a view to defining measures for inhibition of embrittlement (Detroit, (2), p. 3). A later review by Duquette and Stoloff entitled "Aerospace Applications of Intermetallics" has a broader scope, but considerable portions of the text and the 54 references deal with environmental considerations including HE (Paris (9), p. 289). Finally, anyone interested in gaining an understanding of the failure mechanisms is urged to read the review (with 75 references) by Takasugi (MRS IV (12), p. 410). This assessment of integranular fracture addresses various factors affecting the manifestations of such failure (including HE), considering the effects of composition and microstructure. For instance, it seeks to explain the behavior of off-stoichiometry compositions. The latter half of the paper develops mechanisms for the effects of hydrogen and oxygen.

Hippsley and Strangwood have analyzed manifestations of embrittlement by hydrogen and oxygen in the various aluminides (London (7), p. 350).

Iron Aluminides

Liu and coworkers (1989) first reported "An Environmental Effect as the Major Cause for Room Temperature Embrittlement in FeAl." They followed this discovery with the investigation of Fe_3Al, found to be embrittled by water vapor, both in the B2 and DO3 structures (1990a). A later paper (1990b) reported that the embrittling effect of moisture overcomes the beneficial ductilizing effect of boron added to Fe-40 a/o Al.

Gaydosh and Nathal (1990) performed a similar study of FeAl with different aluminum contents in different atmospheres. Shea, Castagna, and Stoloff (MRS IV (12), p. 609) dealt with the role of charging conditions and strain rate on the embrittlement of several Fe_3Al and FeAl alloys. In a review, Liu and McKamey cite work by others including Ni_3Al (see below) and Co_3Ti (Indianapolis (3), p. 133). It is well to also note related work on Ni_3Fe by Camus, Stoloff, and Duquette (1989).

More recent studies of the environmental influence on the behavior of a Fe_3Al-5 a/o Cr alloy (designated FA 129 from Oak Ridge) were presented in poster sessions at MRS V (1992) by Castagna, Maziasz, and Stoloff, as well as McKamey and Lee. The latter determined tensile elongation as a function of the partial pressure of water thus defining a threshold water content required for embrittlement.

Duquette and Stoloff's tri-service review (13) cites recent, unpublished studies that probed factors such as strain rate, method of adding hydrogen (cathodic charging versus gas atmosphere), and alloy composition. For instance, decreasing strain rates result in decreased ductilities in environments containing air or water vapor but have no effect in dry oxygen.

Studies of aqueous corrosion of the iron aluminides include the following:

- Fe_3Al: KASUL and HELDT. Effects of gaseous and aqueous test media on ductility; loss of ductility correlates with hydrogen fugacity, Detroit, (2) p. 67.
- Fe Al: JANAVICIUS and PAYER. Pitting in various aqueous media, Detroit, (2) p. 199.
- Fe_3Al: BUCHANAN and KIM. Pitting: beneficial effects of Cr and Mo. MRS IV, (12) p. 945.

Buchanan has provided a copy of a review chapter prepared for a forthcoming book on intermetallics (edited by Sikka and Stoloff).

Bavarian, et al. studied the environmentally-assisted cracking of Fe_3Al and Ti_3Al. These studies included potentiodynamic polarization measurements and stress corrosion cracking tests (San Diego (10), p. 613).

Nickel Aluminides

The pioneering work was accomplished by Kuruvilla and Stoloff (1985) on Ni_3Al. Their focal concern was HE such as its undoing of the beneficial effect of boron and the effectiveness of a continuous oxide layer as a barrier to the entry of hydrogen. They cite previous work on other intermetallics $(Fe, Ni)_3V$, and Ni_2Cr. Fractography was used to characterize the failure and assist in assessment of mechanical test data which is a practice now quite standard in the field. Their work can be seen as an outgrowth of an earlier study by Berkowitz and Miller (1980) on HE of Ni_2Cr. This study was related to the establishment of the mechanism of HE of Hastelloy C-276; it found a relationship between HE and ordering in Ni_2Cr.

Buchanan and coworkers examined the aqueous corrosion characteristics of three Ni_3Al-derived compositions in a series of electrolytes at 25°C and 95°C. The results are in a final report (1988) to the Nickel Development Institute. Good performance was seen in an assortment of media. Pitting was observed in chlorides.

Dulmaine (MRS III, (11) p. 597) of Carpenter Technology characterized the aqueous corrosion behavior of Ni_3Al with 7.8 w/Cr (designated IC218) in various aggressive media including inorganic and organic acids and basic solutions, comparing it to various commercial stainless steels. In some acids, IC218 compared favorably to common stainless steels. It also exhibited resistance to integranular corrosion and to stress corrosion cracking in 45% magnesium chloride and in acidified brine per NACE TM 0177.

Ricker and his colleagues subsequently published papers on aqueous corrosion of Ni_3Al including electrochemical studies of pitting and passivity and focusing on the role of hydrogen in stress corrosion cracking. They paid attention to factors such as metallurgical condition (annealed versus cold worked) and conditions of hydrogen charging (precharging versus charging simultaneously with slow strain rate tensile testing). These papers appeared as follows:

- RICKER, HALL, and FINK: Includes stress corrosion cracking, relation to hydrogen absorption (1990).
- BERTOCCI, FINK, HALL, MADSEN, and RICKER: Passivity and pitting in various media (1990).
- RICKER, BERTOCCI, and FINK: Cathodically generated hydrogen in various media (Jackson (4), p. 499).
- RICKER, BERTOCCI, FINK, and STOUDT: Various aqueous solutions to elucidate mechanism (Detroit (2), p. 213).

Srivatsan and Sirian compared the tensile behavior of Ni_3Al in several media (Detroit (2), p. 227).

Camus, Stoloff, and Duquette investigated Ni_3Fe and determined its susceptibility to HE; the effect of ordering depends on the conditions of hydrogen charging. The findings are relevant for other intermetallics such as the aluminides. Another distinctive aspect of this study was the preparation of the alloy by pressing and sintering of elemental powders. Residual porosity of about 5% was not seen as a significant factor affecting mechanical behavior (1989).

Titanium Aluminides

Hydrogen embrittlement has probably received more attention for the titanium aluminides (normally the ordered compounds hcp α_2 Ti_3Al and fct γ TiAl) than for all of the other intermetallics combined. Widespread activity continues; the most recent review articles and reports of ongoing research point to the need for further study to provide more test data and diagnoses, to elucidate mechanisms, and to devise preventative or remedial action.

The concise summary in the Duquette and Stoloff tri-service review (13) calls attention to the uniqueness of HE in titanium-base materials; when enough titanium is present (even in the nominally equiatomic TiAl), hydrides are formed. HE is then observed even at temperatures significantly above ambient; for example, 204°C. Very recent reviews were presented by Thompson (Detroit (2) 30 references, p. 21) and later at San Diego (10) (58 references, p. 578). Another recent statement of the mechanisms including hydride precipitation is available in the recently published comprehensive study (with Chu) on Ti-24 a/o Al-11 a/o Nb (1992). A prior report was presented at Jackson (4), p. 543.

The brief review of environmental effects by Eliezer deals predominantly with hydrogen and hydrides (Paris (9), 47 references, p. 321). It includes more recent studies and highlights the significant points. The TiAl is less susceptible to HE than the Ti_3Al but its degradation by hydrogen exposure is still a cause for concern.

The titanium aluminide papers in the September 1989 Jackson Lake Conference on Hydrogen Effects (4) extended the studies to include newer materials and techniques as summarized below:

- SHANABARGER: The interaction of hydrogen at the Ti-24Al-11Nb surface was investigated with Auger spectroscopy and reflected electron energy loss spectroscopy. The conclusions from the respective measurements were that the interaction between the dissolved hydrogen and the Ti_3Al lattice is relatively weak and that the dissolved hydrogen donates electrons to the α_2 conduction band (p. 507).
- CHRISTODOULOU and CLARK: This study showed that XD Ti-45 a/o Al-3 a/oV with 7.5 v/oTiB_2 was insensitive to exposure to hydrogen at 815°C (p. 519).
- ELIEZER, MANOR, and FROES: This study reported cracking in cathodically charged TI-24Al-10Nb-1Mo in the absence of externally applied stresses (p. 523).
- FRITZEMEIER and JACINTO: Ti-14Al-20Nb-3.2V-2Mo (w/o) and Ti-33Al-5Nb-1Ta were tested from -130°C to 204°C in 13.8 MPa and 0.1 MPa helium and hydrogen; the α_2 was susceptible to HE, the γ was not (p. 533).
- COSTA et al: Tritium autoradiography was used to map hydrogen distribution in gas tungsten arc and electron beam Ti-24Al-11Nb weldments. The different distributions of the titanium were correlated with microstructures (p. 555).

At the broader October 1990 Detroit Conference on Environmental Effects (2), Wei and coworkers presented two papers: The first, on the α_2 Ti-24Al-11Nb, analyzed misfit strains between hydrides and the α_2 matrix (p. 47). The second reported an experimental investigation of the reaction of Ti-48Al-1V with hydrogen establishing the solubility and identifying the phases formed (p. 57). This conference also included a study by Kane and Chavachery on exposure of the aluminides to hydrogen gas from 23°C to 815°C (Detroit (2), p. 35). The loss of ductility depended on composition and the conditions of hydrogen exposure; i.e., pressure

and temperature. Bavarian, et al. (San Diego (10), p. 613) studied the environmentally-assisted cracking of Ti_3Al and Fe_3Al, as noted above.

The environmental embrittlement of TiAl was the subject of a thorough study by Takasugi, Hanada, and Yoshida (1992). It was inferred that TiAl in the duplex microstructure (lamellar or equiaxed) has low susceptibility to HE.

Behavior At High Temperatures

Resistance to a high temperature oxidizing atmosphere is absolutely essential for the use of intermetallics in applications seeking to exploit their unique high temperature capabilities; e.g., strength and melting point. Hence, the study of oxidation resistance has a prominent place in the development of these materials. Such studies have been able to draw on the wealth of experience with other materials, notably the alloys used for lower temperature regimes. The underlying theoretical concepts are well established and documented. In addition, techniques and equipment are in place for experimental studies, including characterization of the oxidation products.

The central concept in oxidation of alloys is the selectivity of the oxidation process. The various elemental constitutents differ in their affinity for oxygen; thermodynamic data express these differences quantitatively. The goal then is to achieve an alloy composition that while satisfying other service requirements contains an element capable of forming an oxide coating that serves as an external protective barrier. It has to be continuous (no discontinuities such as pores or cracks), adherent to the substrate even after repeated thermal cycling and self-healing. The challenge of thermal cycling reflects the difference in coefficient of thermal expansion (CTE) between the coating and the substrate As in the current superalloys, relatively small alloy additions such as Zr, Hf, or Y are sought to overcome the problem by improving the CTE match or by helping interlock the coating and substrate, presumably by offsetting the effect of detrimental contaminants. Again, as for current alloys, alloy additions made for other reasons such as strength or reduced embrittlement must also be assessed for their effect on composition and adherence of the protective layer.

The alloying approach derives largely from concepts developed by C. Wagner and is elaborated in the review articles listed below. A relatively recent update of the theoretical treatment is presented by Gesmundo and Viani (1986). Consider an element such as aluminum capable of forming a protective oxide with the desired integrity and sustained protectiveness. It is then possible to define a critical (minimum) concentration above which only this element forms oxide. Bear in mind that other elements in the alloy (or intermetallic) may also be capable of forming oxide thus competing with the desirable element for oxygen. This competition can be particularly keen in aluminides such as those of niobium or titanium (in some cases even nickel) since these other elements have oxygen affinities close to that of aluminum. Luthra (Detroit (2), p. 123) calculated thermodynamic data for the oxides and applied the results to elucidation of the oxidation mechanisms. Another possible source of concern worth noting, although it is less likely to harm the usual aluminides, is that some elements such as silicon and molybdenum form volatile oxides impairing the coating itself or the interface with the underlying metal.

In both tri-service reviews (13) Duquette and Stoloff, as well as Meier and Pettit, go further into the subject and provide references to the experimental data. Meier provides a tutorial review with 29 refeiences emphasizing selective oxidation and achievement of the desired transition from internal to external oxidation (Cleveland (1), p. 1). Another review of his is even more comprehensive (Les Embiez (5), 62 references, p. 1). A noteworthy feature is the attention to the composition of the corrosive medium. Related issues are addressed in Kofstad's keynote lecture at the same symposium (p. 25). More recent reviews by Meier and Pettit (San Diego (10), p. 548; London (7), p. 33) emphasize the current understanding of oxidation behavior.

Oxidation resistance has been a vital factor in the screening of candidate intermetallics for high temperature use. Typically, the selection starts with the requirement of a melting point above 1500°C. General Electric personnel have tested in flowing air in the range of 1000°C to 1500°C (MRS IV (12), p. 969). United Technologies/Pratt & Whitney performed thermal cycling tests to 1149°C or 1200°C (MRS III, (11), p. 361; MRS IV (12), p. 733). Both groups supplement weight change data with analyses of the oxide scales.

Examples will be found below on the effect of the oxidizing atmosphere. Meier and Pettit devote an interesting paragraph to the generalized discussion noting, for instance, the effect of the presence of nitrogen in the atmosphere when pre-oxidation is applied as a protective measure; for example, nitrogen leads to formation of TiO_2-rich scales on TiAl at the expense of the protective aluminide formed in oxygen (see Meier, et al., Cleveland (11), p. 185). It is also worth citing the work of Tortorelli and Bishop on various aluminides in highly oxidizing molten nitrate salt at 650°C (Detroit (2), p. 91).

Niobium Aluminides

The high melting point (1960°C) makes Nb_3Al attractive but oxidation behavior is a serious, even insurmountable deficiency because it cannot form continuous alumina scale. Thus, in both screening studies cited immediately above, United Technologies investigators found severe and rapid oxidation (MRS III (11), p. 361; MRS IV (12), p. 733).

Meier was a member of a team that included NbAl in a more detailed study of the titanium aluminides covered below (Cleveland (1), p. 157). The study sought to improve oxidation resistance by effecting the formation of a protective alumina film. The work was guided by the concept that there is a minimum critical concentration of aluminum for continuous alumina formation. The best overall behavior was exhibited by a composition approximating $NbTiAl_2$ modified with 3 to 5 a/o Cr and V. Such compositional variants have much lower solidus temperatures, making them more acceptable for coatings than for components. Among the many interesting points in this study is the example of the formation of a lower Al phase (in this case Nb_2Al) as a consequence of the initial depletion of Al in oxidation of $NbAl_3$ to form alumina. Such a new Al-deficient phase can manifest its characteristic oxidation behavior with detrimental, even disastrous consequences.

The National Aeronautics Space Administration (NASA) has been investigating $NbAl_3$, an attractive candidate because of its high melting point (1685°C), plus the benefit of high aluminum content on both the density and oxidation resistance (Cleveland (1), p. 171); yet, the oxidation resistance is inadequate and improvements were sought and achieved through alloying guided by the Wagner model. Steinhorst and Grabke reported on the binary $NbAl_3$ with different levels of excess aluminum, investigating oxidation between 650 °C and 1200°C (Les Embiez (5), p. 55). They followed the growth of various oxides accompanying phase changes in the binary. Among the interesting outcomes is the explanation of the internal grain boundary disintegration in the single-phase $NbAl_3$ between 650°C and 1000°C, the phenomenon known as "pesting" with a maximum rate at 750°C. A later publication extending the work to combinations with NiAl and NbNiAl is cited below with NiAl (Liège (6), p. 1703).

Iron Aluminides

Iron aluminides are likely to find use only for limited special applications; they have received modest attention in recent years. Nevertheless, familiarity with them is essential for anyone interested in intermetallics. To begin with, they were the first intermetallics to receive serious attention for substantial application as structural materials as far back as the 1950s. Potentially, cost of ingredients was very low. Oxidation resistance was attractive but brittleness could not be overcome. The renewed interest in intermetallics in recent years had led to studies such as the work by Liu at Oak Ridge clarifying the effects of compositional and environmental factors on ductility. Even if new technology can now improve the position of iron aluminides as engineering materials, their use is restricted by changes in service requirements and advances in the competing alternative materials. Nevertheless, they are of interest since they had led in establishing concepts in the use of intermetallics.

Liu's studies of embrittlement at ambient temperature were summarized above. He has presented an overview paper with 72 references in which the study of the phenomenon is extended to other compositions and higher temperatures (Indianapolis (3), p. 133). The end of the review (p. 146) cites data of Baker and Gaydosh showing ductility of an FeAl alloy to be the same in both air and vacuum from 700°K to 1100°K (see MRS II, v. 81, p. 315).

Shan and coworkers oxidized Fe -22.5 a/o Al-10 a/o Zr glass ribbons at 500°C and investigated the oxides by Secondary Ion Mass Spectroscopy (Detroit (2), p. 133). They incorporated $^{16}O/^{18}O$ tracer studies to help distinguish between stages in the oxidation mechanisms. Two oxide layers were identified.

DeVan has reported encouraging test data supporting possible use of Fe_3Al-base alloys in the sulfidizing environments ($H_2S/H_2/H_2O$) representing coal conversion plants where they could replace more conventional ferrous alloys (Cleveland (1), p. 107; San Diego (10), p. 573). Presumably, corrosion resistance can be improved further by enriching the surface with aluminum.

Smialek, et al. characterized and compared the oxidation behavior of three alloys based on FeAl with NiAl at 900°C, 1000°C, and 1100°C (Cleveland (1), p. 83). The inferior behavior of FeAl was attributed at least in part to the crystallography of the

alumina scale (θ phase versus ∝ phase with corresponding morphological differences) and to larger CTE mismatch stresses.

Nickel Aluminides

The nickel aluminides, fcc Ni_3Al and bcc NiAl, have been prominent among intermetallics considered for high temperature applications. Ni_3Al is a candidate material for structural components; NiAl is also promising for coatings. The former (γ') has a long history as the dominant constituent of the widely used nickel-base superalloys; hence, a substantial information base is available.

The previously cited review by Liu extensively covers the oxidation of Ni_3Al and cites work by others as well as himself (Indianapolis (3), p. 133; especially, p. 141f). Liu's concern is not with the usual manifestations of oxidation (weight change, scale formation, and loss), but rather with the effect of even small amounts of oxygen on mechanical behavior such as embrittlement, fracture mode, crack propagation, pre-oxidation, and grain size. These last two issues receive attention in later (or concurrent) publications on Ni-23Al-0.5Hf-0.2B designated IC50 by Oak Ridge (MRS III (11), p. 293; Takeyama, 1989). A more recent review is available by Takeyama and Liu (San Diego (10), p. 538). DeVan and Hippsley (Cleveland (1), p. 31) established the susceptibility of Ni_3Al to embrittlement by internal oxidation at 600°C to 825°C. The IC50 was used by Natesan (1989) for a comprehensive study of oxidation and sulfidation. Much of the earlier work is summarized by Stoloff (1989; especially, p. 179f). Attention must be paid to the diversity of compositions studied. Examples include the 0.5 w/o Y used with Ni_3Al by Kuenzly and Douglass (1974) over the range of 900°C to 1200°C in air and 0.1B, plus 2 a/o Ti, Zr, or Hf by Taniguchi, et al. (1986). A later publication also included 2 a/o Cr (Cleveland (1), p. 7). The basic Ni_3Al, designated NiAl 11 by VDM, was cycled between 750°C and 1100°C by Brill and Klower in the following atmospheres: oxidizing, carburizing, sulfidizing, and chloridizing. The aluminide was compared with commercial alloys used in these atmospheres (MRS IV (12), p. 963). Jiangting, et al. investigated the oxidation behavior of the Ni_3Al + 8 Cr + 0.1 B alloy with Zr addition over the range of 850°C to 1150°C (MRS III (11), p. 591). Single crystal Ni_3Al was oxidized at 950°C at low oxygen partial pressure by Schumann, et al. (MRS IV (12), p. 951).

As an interim final word on Ni_3Al, attention is again drawn to Takasugi's review of intergranular fracture, cited above for HE (MRS IV (12), p. 410). In his brief treatment of oxygen as dopant/contaminant that interacts with boron and carbon, the data of Takeyama and Liu (1989) were used.

The corrosion resistance of NiAl is sufficiently outstanding for it to be used as the starting composition for coating materials, while lack of ductility hampers its use for components. For an overall review of NiAl with 51 references, refer to Darolia (1991). In fact, NiAl can probably be considered the progenitor of the (Ni, Co) Cr, Al, and Y family of coatings now standard for superalloys. A helpful review (59 references) of these and other high temperature coatings was presented by Mevrel (Les Embiez (5), p. 13). A more recent review is available by Rickerby and Winstone (1992). Several recent studies of NiAl are noted below.

Rybicka and Smialek (1989) thoroughly investigated the oxidation behavior of NiAl + Zr over the range 800°C to 1250°C devoting particular attention to the nature of the Al_2O_3 scale including its phase transformations. The oxide scale received similar attention from Doychak, Smialek, and Mitchell (1989) in a study of single crystal NiAl. The benefit of Zr doping had been shown in previous work at NASA (see Barrett, Cleveland (1), p. 67). A related study was done by Doychak, Smialek, and Barrett (Cleveland (1), p. 41). A more recent treatment by the NASA group including both Barrett and Doychak extends the aluminum oxidation to the depletion of aluminum, producing Ni_3Al and leading to less protective $NiAl_2O_4$ (San Diego (10), p. 561). Related work on ion implantation with yttrium has been reported (Jedlinski and Mrowec, Marseille (8), p. 281; Pint, Jain, and Hobbs, MRS IV (12), p. 981). Both groups used sophisticated techniques of surface diagnosis to help elucidate the oxidation mechanism. The Polish workers also compared single crystal and polycrystalline NiAl; rates were considerably lower for single crystals. It was found that the presence of yttrium improved the scale adherence and reduced the scale growth rate. These benefits were attributed to the elimination of inward diffusion of oxygen. Pint, et al. found that the effects of yttrium on adherence and rate were not necessarily beneficial and depended on the oxidation temperature. Any treatment of the oxide growth mechanism has to consider the work of Nicholas-Chaubet, et al. who used similar diagnoses but relied heavily on scanning electron microscopy (SEM) observations of oxide morphology, notably a pattern of ridges, to formulate a multistep growth process (Les Embiez (5), p. 83).

Sulfidation resistance is expected of NiAl-based coatings in service in a "hot corrosion" atmosphere. Godlewska, Godlewski, and Mrowec studied behavior of NiAl-Cr pseudobinaries at 800°C to 1000°C in sulfur-containing atmospheres (Marseille (8), p. 183, Cleveland (1), p. 147). The various sulfides in the scales included liquid sulfidation products. The scales were nonprotective leading to sulfidation rates that exceeded oxidation rates by several orders of magnitude.

Further work on compositions derived from NiAl is described in two interesting papers at the September 1990 Liège conference on High Temperature Materials for Power Engineering (6) (see final section of Symposium Proceedings). The paper by Singheiser, et al. of ABB (p. 1687) is a fairly broad review of the environmental behavior of several categories of intermetallics including the NiAl/$NbAl_3$ work of the next paper. A particularly interesting section refers to the addition of Cr at different levels (up to 38.5 w/o) to NiAl for improved hot corrosion resistance. The various oxide scales were characterized. The paper by Grabke, et al. of the Planck Institute in Düsseldorf presents the results of an extensive study of oxidation in the range of 1000°C to 1200°C for a series of compositions based on $NbAl_3$, NiAl, combinations of the two, and a multiphase combination of the two with NbNiAl (p. 1703). They identified a promising three-phase combination consisting of 39 v/o NbAl, 46 v/o NiAl, and 15 v/o NbNiAl. Another detailed report on this study is now available (London (7), p. 339).

NiAl is receiving attention as the matrix for composites. Pregger, et al. reported oxidation studies on Martin Marietta's XD with 10 or 20 v/o Ti_2B in NiAl: the Ti_2B impairs corrosion resistance (San Diego (10), p. 567). In their tri-service review Duquette and Stoloff cite unpublished data on enhanced corrosion resulting from additions of HfB_2 or Ti_2B.

Titanium Aluminides

The titanium aluminides offer an attractive combination of properties; the densities are made relatively low by the presence of two low density elements. The melting points (solidus temperatures) progressively decrease with increasing aluminum content from Ti_3Al (α_2) to TiAl (γ) to $TiAl_3$, but the 1340°C solidus of $TiAl_3$ is hardly a restrictive factor. However, as for all titanium base compositions, oxidation can set an upper limit for service temperature. The higher concentration of aluminum offers a means of achieving protection through its formation of alumina. The presence of significant concentrations of both aluminum and titanium presents a particular challenge/opportunity since the two elements are close in oxygen affinity. Indeed, aluminum had the greater affinity but its advantage in the competition for oxygen can be overcome by titanium depending on circumstances; see, for instance, interaction studies of Misra, 1991. The challenge is then to make the oxidation so selective that it generates only alumina entirely at the surface where it maintains its integrity and adhesion for the required protection against further oxidation. Thus, effort has been devoted to ternary alloy additions to improve the stability of the protective oxides.

Welsch and Kahveci oxidized the following series of compositions in dry oxygen between 600°C and 1100°C: Ti_3Al, TiAl, an intermediate two-phase composition, and Ti_3Al plus niobium (Cleveland (1), p. 207). Lee and Waldman (1988) oxidized a single alloy containing both Ti_3Al and TiAl from 400°C to 1500°C in air; the three oxides (Al_2O_3, TiO_2, and Al_2TiO_5) found in surface scales and internally within the metal were identified. Umakoshi, et al. (1989) identified the oxides formed on TiAl and $TiAl_3$ from exposure to oxygen from 800°C to 1000°C. Meier, Perkins, and coworkers included binaries containing 26 to 64 a/o Al in studies in oxygen and air over the range 800°C to 1300°C (Cleveland (1), p. 185).

Binaries containing 48 a/o Al and 52 a/o Al were included by McKee and Huang in their alloying studies (see MRS IV (12), p. 939). Shimizu, et al. reported data on bare TiAl as part of their study of coatings (San Diego (10), p. 602).

Alloying of Ti_3Al almost always involves niobium for improved mechanical properties, high temperature, strength, and low temperature ductility. A review with 45 references was presented by Rowe (Indianapolis (3), p. 375). Welsch and Kahveci included Ti_3Al-21.2 a/o Nb in the oxidation studies cited above (Cleveland (1), p. 207). The alloy Ti-24 a/o Al-11 a/o Nb has been the subject of studies by Balsone (Cleveland (1), p. 219); Sankaran (1990); Wiedemann (Cleveland (1), p. 195) and coworkers; and Parida and Nicholas (1992). The first two were more concerned with crack growth. A later publication by Sankaran and others in the NASA Langley group dealt with Ti-25 Al-10Nb-3V-1Mo (Wallace, 1990). Singheiser, et al. reported on the benefits of silicon added to Ti_3Al with and without niobium; they performed cyclic oxidation tests in air to 850°C (Liège (6), p. 1687). Promising oxidation behavior was reported by Wagner, et al. on an alloy containing niobium and based on the eutectic of α_2 Ti_3 (Al, Si) and the silicide Ti_5 $(Si, Al)_3$ (MRS IV (12), p. 1007).

A new alloy family derived from Ti_3Al and containing silicon at several levels; e.g., 0.9 a/o was reported recently. (In his review at the 1992 MRS conference,

Lipsitt cited attractive mechanical behavior reported by Kerry, et al. at the 1992 World Conference on Titanium.) Lipsitt includes environmental behavior as among the properties yet to be characterized for the new composition. It is worth noting Lipsitt's general comment that the Ti_3Al-base alloy will require a protective coating.

Rowe has presented data on another family of alloys that evolved from niobium-rich Ti_3Al (Indianapolis (3), p. 375; Paris (9), p. 61). These alloys are based on Ti_2AlNb and have a new orthorhombic structure. Mechanical properties appear better than for α_2 Ti_3Al but little has been reported on environmental behavior.

A considerable number of studies have been reported on alloy additions to TiAl: Perkins, Meier, and their colleagues were guided by the Wagner model in adding Re, Mo, Cr, W, V, and Nb (Cleveland (1), p. 157). Tests were performed in air at 1100°C to 1400°C and in oxygen at 800°C to 1100°C. Attractive behavior was found in alloys approaching $TiNbAl_2$ modified with 3 to 5 a/o Cr. Nishiyama, et al. found additions of V, Nb, and W beneficial while Mn was detrimental (Indianapolis (3), p. 557). Wallace, et al. investigated the alloy Ti-33 w/o Al-6 w/o Nb-1.4 w/o Ta in air from 700°C to 1000°C (Detroit (2), p. 79). They noted the formation of the nitride phases TiN and Ti_2AlN on specimens exposed in air.

McKee and Huang evaluated alloys with 48 a/o Al or 52 a/o Al and also included additions of Cr, Ta, Nb, or W to the 48 a/o alloy (MRS IV (12), p. 939). The alloys were cycled in flowing air to 850°C and 1000°C. They have also submitted later reports on such alloys. One study (Huang 1991) showed ductilization by chromium and improvement of oxidation resistance by niobium. This study led to identification of Ti-48Al-2Cr-2Nb as an attractive composition. The other study (McKee, 1992) dealt with oxidation behavior at 850°C to 900°C and showed that in addition to Cr and Nb, the Cr and Ta, Mn and Ta, and Mn and W combinations significantly increase oxidation resistance. One such composition, Ti-Al 45-56 Cr 1-4 Ta 4-8, was so oxidation resistant that it was patented for use as a coating (U.S. 5, 149, 497).

Maki, et al. studied the effects of Si and Nb individually and in combination; tests were in flowing air between 700°C and 950°C (San Diego (10), p. 591). In combination, the two elements more effectively increased the oxidation resistance. Chen, et al. investigated a wide range of compositions in the Ti-Al-Nb system in static air from 900°C to 1200°C (San Diego (10), p. 597). It was established that the composition region with the best oxidation resistance (Al = 55 to 64 a/o and Ti/Nb (a/o) = 2.5) is not consistent with the region for highest strength. The reviews by Duquette and Stoloff cite unpublished data on additions to Ti-Al, notably Nb, with significant improvements in oxidation resistance.

Luthra performed thermodynamic calculations relevant to the stabilities of various phases as affected by the presence of Ni, Cr, and Si (Detroit (2), p. 123). The stability of the oxide phases depends on the activities of Ti and Al in the Ti-Al phase. Rahmel and Spencer (1991) have calculated the metal activities in the Ti-Al system and have used the results to predict oxide stability. Misra (1991) characterized the interaction of alumina with a series of Ti-Al alloys containing aluminum over the range 0 to 54 a/o at temperatures from 900°C to 1300°C. The work was directed primarily to the use of alumina fibers as reinforcement in Ti base matrices,

but Misra also considered the implications for oxidation behavior of Ti-Al alloys with the conclusion that the titanium content has to be kept low enough (as in TiAl) to prevent it from having sufficient activity to remove oxygen from the alumina.

Two publications from the San Diego Conference (10) report applications of sophisticated analytical techniques. Taylor and Paffett performed a surface study including X-ray photoelectron spectroscopy and secondary ion mass spectroscopy on the progressive development of oxides on TiAl-2 a/o Nb (p. 584). Shanabarger used Auger electron spectroscopy to follow the initial oxidation of Ti_3Al and TiAl at room temperature (p. 608). Taylor and Paffett reported further work with such surface probes in a poster session at MRS V (1992).

Reports on titanium aluminide matrix composites are limited. In a thorough review of Ti-24 Al -11Nb as the matrix for SiC-reinforced composites, MacKay, Brindley, and Froes (1992) identify environmental resistance as a "show stopper." The Duquette and Stoloff tri-service review (13) cites unpublished data on different increases in static oxidation rates for TiAl reinforced with different oxides.

Coatings

Various coating approaches have been investigated for protecting titanium aluminides by preventing access of oxidizing atmospheres. The barriers include oxide, aluminum-rich layers, and oxidation-resistant intermetallics.

Kobayashi, Yoshihara, and Tanaka (1990) improved the oxidation resistance of TiAl by pre-oxidation in low partial pressure oxygen, presumably forming a protective Al_2O_3 layer. Wiedemann, et al. achieved protection of Ti-24 Al-11Nb with oxides prepared from prior surface application of sol gels (Cleveland (1), p. 195; Detroit (2), p. 107).

A titanium-base material can be enriched with aluminum at the surface to obtain the resistant $TiAl_3$ as noted, for instance, by Umakoshi, et al. (1989) in their studies of TiAl and $TiAl_3$. Subrahmanyam (1988) pack aluminized Ti-14 w/o Al-24 w/o Nb and found improved behavior in cyclic oxidation experiments at 1000°C and 1100°C. Mabuchi, et al. (1989) pack aluminized TiAl and identified the $TiAl_3$ at the surface. It is also noted that subsequent interdiffusion led to the formation of $TiAl_2$. Mishuyama, et al., in an engineering study of TiAl turbocharger rotors, expressed commitment to aluminizing on the basis of initial tests but pointed to the need for the process to "be improved much more before going into mass production" (Indianapolis (3), p. 637). Yoshihara, Tanaka, Suzuki, and Shimizu (MRS IV (12), p. 975) combined pre-oxidation and aluminizing and reported excellent resistance to cyclic oxidation in air to 950°C.

Externally applied coatings (versus the above conversion coatings) can be derived from within the Ti-Al system. One such coating is the Ti-Al 46-56 Cr 1-4 Ta 4-8 patented by McKee and Huang (U.S. 5, 149, 497).

Titanium-base materials can also be coated with MCrAl-type alloys such as those used on nickel-base superalloys (Luthra and McKee, U.S. 5, 077, 140); in these coating alloys, M represents Fe, Co, and/or Ni in combination with the oxide formers Cr

and Al. McKee has increased the effectiveness of such coatings by interposing a one-micron-thick or two-micron-thick sputtered barrier of Cr or W (MRS V, 1992). Shimizu, et al. sprayed Co-32 Ni-21Cr-8Al-0.5Y to obtain lower cyclic oxidation rates comparable to those of nickel-base superalloys to 900°C (San Diego (10), p. 602).

Multiyear programs on coatings are underway under U.S. Air Force sponsorship at three gas turbine manufacturers: Allison, Garrett, and General Electric. The programs include both α_2 and γ compositions, but each engine company has its own choice of compositions representing the two Ti-Al phases. Similarly, the coatings being investigated differ in the three programs. Not enough information is available on these programs; however, completion of these programs should permit (1) assessment of the prospects of achieving practical protection of these intermetallics, and (2) narrowing the choice of approaches worth pursuing for production.

Assessment

The development of intermetallics is dominated primarily by the search for satisfactory mechanical behavior. This behavior is the critical issue that will determine the extent of utilization of intermetallics. Environmental effects have to be considered but have received lower priority. The history of the intermetallics shows the importance of recognizing the more subtle effects of the environment, notably on integranular fracture. The understanding and elimination of these effects can be viewed as part of achieving the desired mechanical behavior; low level additions are sought to immunize the compounds against environmental embrittlement. Besides reducing the mechanical capability of the compounds, the environment can cause more gross effects, consuming the compound by converting significant portions to oxide.

As for other metals, two approaches are available for reduction of detrimental environmental reactions: (1) overall modification of the composition, and (2) surface application of barrier materials (protective coatings). It is not desirable, or even necessary, to defer pursuit of these approaches pending the definition of compositions that prevail because of mechanical behavior. It is appropriate to define and address the issues. The contributing factors can be understood and the technology established for eventual application to the compositions that will prevail. For now, it is not necessary to know the final compositions; it is only necessary to select representative compositions for investigation.

The dominant systems are Ni-Al and Ti-Al. Two choices are available for both: M_3Al or MAl. In each case, the high aluminum compound NiAl or TiAl is inherently more oxidation resistant, but the eventual choice is likely to be based on other considerations.

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